Oil Shale, 2000, Vol. 17, No. 3
pp. 261-265
ISSN 0208-189X

https://doi.org/10.3176/oil.2000.3.07

STUDY ON PRODUCTION OF LOW-SOLIDIFICATION-POINT FUEL OIL FROM FUSHUN SHALE OIL

Y. H. ZHAO

Oil Shale Refinery, Fushun Mining Administration
Fushun, 113008, China

The characteristics of Fushun shale oil were analysed in view of its current status, as Fushun shale oil is now only being used directly as boiler fuel, and considering the market requirements for low-solidification-point fuel oil. Research work to find the way of producing such fuel from Fushun shale oil has been done. The methods of adding depressant, adding diluents and catalytic cracking have been tested. The results are discussed in this paper.

Introduction

Approved by the National Plan Committee of China, Fushun Oil Shale Refinery was built in 1989. Now the annual capacity for producing shale oil reaches 90,000 tonnes. Shale oil is produced by retorting of oil shales [1]. Organic matter in oil shale is decomposed by heating. It is a mixture of various organic compounds. It contains a great deal of hydrocarbons as crude oil; but crude oil is mainly composed of saturated hydrocarbons. It can be processed and refined easily, and its products are relatively stable [2]. Shale oil contains many organic heterocyclic compounds with nitrogen and oxygen, and also many unsaturated hydrocarbons [1] what makes the properties and composition of shale oil more complicated and, consequently, its processing and refining more difficult. Shale oil obtained in our refinery is sold only as boiler fuel.

As Fushun shale oil has high solidification point, it does not meet the market requirements for low-solidification-point fuel oil of higher price. Besides, that oil not only has a high content of light fraction, but the calorific value of the latter is also higher than that of the residual crude oil. So, the marketing of shale oil as boiler fuel is not the best solution. Therefore the research work on the production of low-solidification-point fuel oil from the Fushun shale oil has been carried out.

Composition and Properties of Shale Oil

Table 1. **Physical and Chemical Properties of Fushun Shale Oil**

Parameter	Value
Density d	0.9033
Tar acid, vol.%	3.7
Tar base, vol.%	2.5
Kinematic viscosity $\nu_{50\,°C}$	10.3
Solidification point, °C	33.0
Content of wax, %	20.2
Content of asphalt, %	0.85
Gum, %	42.0
Ash, %	0.08
Distillation range, °C:	
Initial boiling point	216
10 %	264
20 %	293
30 %	318
40 %	343
50 %	362
Elemental analysis, %:	
Carbon	85.39
Hydrogen	12.09
Sulfur	0.54
Nitrogen	1.27
Oxygen	0.71
Carbon/hydrogen, wt ratio	7.06
Calorific value, kJ/kg	45980

Fushun shale oil contains much nitrogen compounds, its nitrogen content reaches 1.27 %. The oil is brown, ointment-like under normal temperature, and smells irritatively. Gasoline fraction accounts for 2.5–2.7 %. Fraction before 360 °C accounts for about 40–50 %. The heavy fraction, together with the wax, accounts for 25–30 %, and residual oil – for about 20–30 %. The large amount of paraffins in shale oil causes a high solidification point. The content of asphalt is low. In a word, it belongs to the paraffin-base oil with high nitrogen content.

The characteristics of Fushun shale oil are given in Table 1. The heavy fraction of shale oil contains much paraffin hydrocarbons. The paraffins are separated from shale oil by using successive crystallization method. The alkanes of C_{18} to C_{41} with melting point from 28 to 83 °C are mainly composed of normal hydrocarbons, while isoalkanes account for about 20 % only. The composition of paraffins in Fushun shale oil has been determined as shown in Table 2.

Experimental

Solidification point of shale oil is 33 °C. It solidifies at the normal temperature. At present, there are a few methods of lowering solidification point of oil discussed below.

Adding Pour-Point Depressant

In general, when temperature is lowered, the oil solidifies, mainly due to the crystallization of paraffin wax, also due to the increasing viscosity of oil. When a pour-point depressant is added to the shale oil, with lowering the temperature, the paraffin molecules attach to the long hydrocarbon chain of the depressant. It changes the direction of the paraffin wax crystallization, prevents the wax crystal growth, and destroys the crystalline structure. Paraffin crystals are very small and these very small crystals cannot unite together to form a unite structure, thus solidification is prevented.

At present, there are many kinds of depressant in the market; most of them are fit for diesel oil, and some fit for crude oil. The screening of depressants is complicated and difficult. The properties of shale oil are different from those of diesel oil and crude oil, too. The way of adding different depressants produces little effect.

The laboratory results of adding large amounts of depressants are shown in Table 3. As shown in Table 3, this method is not practical, the effect is not significant, and it costs much.

Table 2. **Composition of Paraffins in Fushun Shale Oil**

Melting point, °C	Density	Molecular formula	Content, wt%
80.6	0.7892	n-$C_{41}H_{84}$	2.1
72.5	0.7821	n-$C_{34}H_{70}$	2.7
68.3	0.7784	n-$C_{32}H_{66}$	1.4
65.5	0.7762	n-$C_{29}H_{60}$	5.6
63.5	0.7746	n-$C_{28}H_{58}$	6.6
59.4	0.7719	n-$C_{27}H_{56}$	9.1
57.2	0.7704	n-$C_{26}H_{54}$	8.1
54.8	0.7681	n-$C_{25}H_{52}$	6.2
53.6	0.7670	n-$C_{24}H_{50}$	7.6
51.5	0.7653	n-$C_{23}H_{48}$	6.2
47.2	0.7625	n-$C_{20}H_{42}$	8.2
36.5	0.7550	n-$C_{18}H_{38}$	3.7
78.8	Not det.*	i-Paraffin	0.6
71.5	"	i-Paraffin	0.2
61.8	"	i-Paraffin	0.4
49.8	"	i-Paraffin	0.9
44.3	0.7822	n-$C_{26}H_{54}$	6.5
39.9	Not det.	n-$C_{25}H_{52}$	3.1
28.9	0.7816	n-$C_{24}H_{50}$	3.8
22.6	Not det.	n-$C_{24}H_{50}$	1.3

* Not determined.

Table 3. **Experiments with Depressant Addition**

Added, wt%	Solidification point, °C	Temperature lowering, °C
Depressant A		
2	30	3
4	25	8
6	22	11
Depressant B		
2	26	7
4	21	12
6	19	14
Depressant C		
1	28	5
3	25	8
5	20	13

Mixing with Diluent Oil

The method of mixing with diluent oil is a popular method, applied in refineries for improving the quality of oil products. Besides, the depressant may also be added.

Experiment is conducted as follows:

- Adding diluent and depressant to the shale oil with a certain definite ratio
- Heating and stirring the mixture
- Analysing

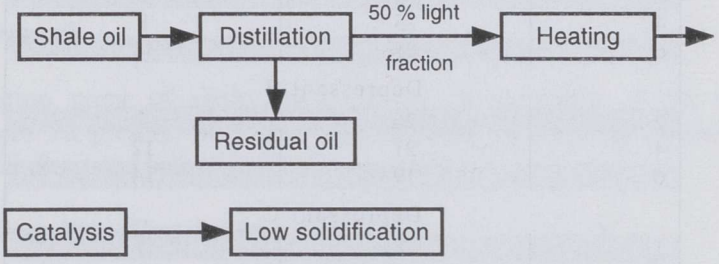
Table 4. **Lowering of the Solidification Point by Adding of Diluent**

Addition	Added, wt%	Solidification point, °C	Temperature lowering, °C
Depressant A			
Diluent Depressant	15 0.05	25	8
Depressant B			
Diluent Depressant	20 0.08	21	18
Diluent Depressant	25 0.10	18	18
Depressant C			
Diluent Depressant	30 0.15	17	16

The results given in Table 4 show that the solidification point can be reduced to 17–18 °C by adding 25–30 % diluent, and 0.08–0.1 % depressant, but this effect is not satisfactory, especially for the use in winter. Addition of more diluent is not applicable, due to the higher cost.

Catalytic Depressing of Solidification Point

Shale oil is fractionated, and 50-% light fraction is obtained. Its solidification point is 21 °C; this light fraction is passed through a catalytic cracking fixed bed, filled with the catalyst CTL-1 (developed by Fushun Research Institute of Petroleum and Petrochemicals). Technological process of this method is shown in the Scheme below.



The distilled and residual oil have been analysed, the results are presented in Tables 5 and 6, respectively. From Table 5 it is seen that the quality of the 50 % light fraction of shale oil completely meets the requirements for the marine fuel oil. The properties of residual oil meet the fuel oil quality standard except the flash point (Table 6). It may be mixed with shale oil and sold as boiler fuel. This technology is simpler, and the marine fuel has a great market potential and also a higher price.

Table 5. **Properties of Light Fraction**

Indices	Marine fuel oil standard	Analytical data of light fraction
Kinematic viscosity at 20 °C, mm^2/s	3–8	4.74
Flash point (open cup), °C, not lower	80	83
Solidification point, °C, not higher	0–5	–2
Sulfur content, %, not higher	0.3	0.27
Ash content, %, not higher	0.1	None
Water content, %, not higher	0.3	Trace
Density at 20 °C	As measured	0.8521

Table 6. **Properties of Residual Oil**

Indices	Fuel oil quality	Analytical data of residue
Kinematic viscosity at 50 °C, mm^2/s	15	13.8
Flash point (open cup), °C, not lower	110	99
Solidification point, °C, not higher	35	35
Ash content, %, not higher	0.3	0.25
Water content, %, not higher	2.0	Traces
Mechanical impurities, %, not higher	2.0	1.0

Conclusions

(1) Fushun shale oil belongs to paraffin-base oils, its solidification point is high, and it is now sold only as boiler fuel.

(2) Three methods for lowering the solidification point have been investigated. Among them, distillation followed by catalytic cracking for making marine fuel is suitable for our refinery. At first, we only need to build a small installation for distillation and catalytic cracking to upgrade the shale oil to get a 50-% yield of marine oil. In this way, we can produce a qualified marine oil with higher price, and if we decolorize the product, we can obtain diesel oil and get even more benefit.

REFERENCE

1. *Hou X. L.* Shale Oil Industry of China (English edition). – The Hydrocarbon Processing Press, Beijing, 1986.
2. *Lin S. X. et al.* Petroleum Refining Engineering. – Petroleum Industry Press, Beijing, 1981 [in Chinese].

Presented by Jialin Qian
Received January 21, 2000